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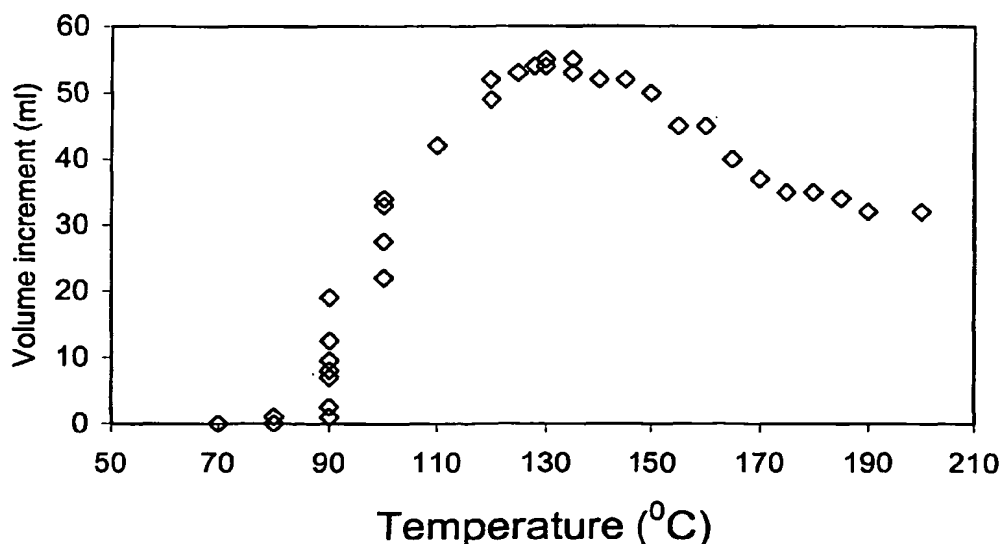
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(54) Title: TOUGHENING OF THERMOSETS



(57) Abstract: A method of manufacturing thermosets such as epoxy resins includes adding expandable hollow microspheres, which expand with temperature as shown in the accompanying graph, to the base thermoset components in the liquid phase and applying heat treatment to the mixture so formed causing the microspheres to expand during or after curing of the thermoset. This results in a toughening mechanism caused by compressive residual stress around the microspheres which significantly increases the specific fracture energy of the epoxy resin.



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For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

TOUGHENING OF THERMOSETS

FIELD OF THE INVENTION

This invention relates to the toughening of thermosets and has been devised particularly though not solely for application to epoxy resins.

5 BACKGROUND OF THE INVENTION

Thermosets, such as epoxy resins, are brittle compared to thermoplastics because of their cross-linked molecular structures. Attempts have been made in the past to increase the toughness of thermosets, particularly epoxies, using the addition of liquid rubber or hard particles.

10 Liquid rubber has been successfully used as a toughening agent to increase the specific fracture energy. Its toughening mechanisms include bridging, cavitation, crack pinning, crack blunting etc. In addition to liquid rubber, other toughening agents such as hard particles, hard hollow microspheres and coreshell rubber have also been used.

Another development in this area is an attempt to toughen thermoplastics using a
15 similar method to the one used for ceramics in which toughness increase was achieved by a volume dilatation in the vicinity of crack tip resulted from tetragonal to monoclinic phase transformation.

The present invention results from the realisation that the pre-stressing of the epoxy matrix, and the creation of residual compressive stress may be performed using expandable
20 hollow microspheres and heat treatment to achieve a similar effect to that of the phase transformation of ceramics.

SUMMARY OF THE INVENTION

Accordingly, the present invention provides a method of manufacturing thermosets including the steps of adding expandable hollow microspheres to at least one of the base
25 thermoset components in the liquid phase, and applying heat treatment to the mixture so formed, causing the microspheres to expand during, or after, curing of the thermoset.

Preferably the thermoset comprises an epoxy resin and the microspheres are added to the epoxy component.

Preferably the mixture of epoxy component and microspheres are heated before
30 adding a curing agent.

Preferably the mixture is allowed to cool before adding the curing agent.

Preferably the mixture is stirred after adding the curing agent, and poured into a mould to cure.

Preferably the microspheres include a co-polymer shell and gas.

BRIEF DESCRIPTION OF THE DRAWINGS

Notwithstanding any other forms that may fall within its scope, one preferred form of the invention will now be described by way of example only, with reference to the accompanying drawing which is a graph of the volume incremental expansion of
5 microspheres due to heating.

DETAILED DESCRIPTION OF PREFERRED EMBODIMENTS OF THE INVENTION

In the preferred form of the invention, a thermoset in the form of an epoxy resin is toughened by the addition of expandable hollow microspheres, but it will be appreciated that this method can be applied to any other form of thermoset material.

10 A conventional resin system such as the resin system consisted of West System Epoxy 105 (a blend of Bisphenol A and Bisphenol F) and West System Slow Hardener 206 (a blend of aliphatic amines and aliphatic amine adducts based on diethylene triamine and triethylenetetramine) as curing agent, has a typical density of 1.1 for the resin system.

The system can be modified by the addition of expandable hollow microspheres as
15 demonstrated in the following example.

Modifier used was hollow micro-spheres (EXPANCEL, 551 DU40, Akzo Nobel) which consist of co-polymer shell and gas. The chemical structure of the microspheres was found to be $(C_5H_8O_2-C_3H_3N-C_2H_2Cl_2)_x$ using a Perkin Elmer Fourier Transform Infra Red Spectrometer, Paragon 1000. The microspheres expand when heated. By way of
20 example, microspheres were put in a 100 ml measuring cylinder and tapped for 5 minutes and then placed in an oven pre-heated to 70°C. Further heating of the oven followed every 5 to 6 minutes for an increment of 10°C until it reached 200°C. Resulting volume expansion of the microspheres measured as a function of temperature is shown in the accompanying diagram.

25 In a typical method of manufacture, a quantity of microspheres are added to the epoxy component and stirred for approximately ten minutes. The mixture is then heated to approximately 85°C for thirty minutes to reduce the viscosity for easy stirring before being allowed to cool gradually e.g. in a water bath for about half an hour. The curing agent is then added and stirred for five minutes.

30 The mixture can then be poured into a casting mould and left to cure at room temperature.

Comparative Testing

Four different types of specimens were prepared viz pure epoxy (PE), heated pure epoxy (HPE), micro-sphere modified epoxy without heat treatment (ME), and micro-

sphere modified epoxy with heat treatment (MEH). The HPE was to check any change in properties of PE due to heating which was also applied to MEH. The ME was to be used in comparison with MEH for checking any heat treatment effect on MEH.

The mixing of epoxy and curing agent was conducted by stirring for five minutes.

5 The stoichiometric amount of curing agent was 17 phr (by weight) for all specimens. The mixture was poured into an aluminium mould with 6 mm thick cavity and left for curing at room temperature at least for one day. Temperature rise in the mould due to exothermic reaction was monitored using a thermocouple and found to be about 8°C which does not much effect the expansion of micro-spheres (see accompanying drawing).

10 For both ME and MEH, a 10 phr of 551 DU was added to epoxy and stirred for about 10 minutes. This mixture was heated to approximately 85°C for 30 minutes to reduce the viscosity for easy stirring and then allowed to cool gradually in a water bath for about half-hour. The hardener was then added and stirred for 5 minutes. The casting was conducted in the same way as for PE and HPE.

15 The heat treatment was conducted for HPE and MEH. Both HPE and MEH was heated in an oven at 135°C for one hour and then allowed to cool down to room temperature. Further two hour heating was conducted at the same temperature for 2 hours.

Results of the four different types of specimens for fracture toughness, flexural elastic modulus and flexural strength are listed in Table 1. Elastic modulus of PE appears

20 to be not much affected by heat treatment and modification with hollow microspheres. Also its flexural strength appears to decrease due to modification without heat treatment but to a lesser extent when the modification is accompanied by the heat treatment. Fracture toughness, however, increases due to both modification and heat treatment. The increase of PE in fracture toughness after heating may be due to post-curing effect,

25 although fracture surface features of HPE appeared to be different from that of PE.

Microscopic work was conducted to identify toughening mechanisms of ME and MEH. During preliminary observation of SEM images, some differences between MEH and ME were found. Some debonding between microspheres and matrix was found in ME, which is different from that of hollow latex particle with a styrene-acrylic shell, and some

30 microspheres were pulled out. In contrast, MEH did not display any gaps between microspheres and matrix, and cracking passed through the microspheres without any pull-out of microspheres.

When MEH is heated, it is found that microspheres naturally expand against the matrix resulting in both matrix, and subsequently microspheres would permanently deform

- 4 -

if deformation is sufficiently high. Consequently, residual compressive stresses around microspheres are created when cooled down. In order to confirm the residual compressive stress in the matrix, a thin section of MEH was examined and the residual stress was indeed found to exist around microspheres. The fringe patterns are observed around microspheres as evidence of the residual stress.

The effect of compressive stress in the vicinity of a crack tip is well known. In the case of ceramics toughening, the compressive stress is produced by localised volume dilation in the vicinity of crack caused by phase transformation. In the case of MEH, however, the compressive stress is distributed around microspheres throughout the whole specimen. Contribution of each microsphere to the toughness increase depends on its location – the closer to the crack tip, the more contribution.

Further to check if the residual stress in MEH is due solely to heat treatment, a thin section of ME was also examined and residual stress around microspheres was found as well. An epoxy shrinks during curing and thus it seems that the residual stress was caused by shrinkage in this case since it was not subjected to heat treatment. Accordingly, it appears that toughness increase in both ME and MEH were affected by the compressive residual stress. Quantification of the residual stress was not attempted, but the residual stress in MEH should be higher than in ME because the residual stress due to the epoxy shrinkage applies to both MEH and ME, and hence the residual stress in MEH would be the result of additional contribution of matrix shrinkage. Also, it had been observed using photo-elastic photos that there is generally much higher residual stress in MEH than in ME.

No gaps between microspheres and matrix in the vicinity of the crack tip were found in fast cracking regions for both ME and MEH. This suggests the gaps of ME are due to the cavitation when the crack slowly propagates. However, the absence of gaps in MEH indicates that, if bonding between microspheres and matrix is not sufficiently strong, there was no cavitation.

30

Material	K_{IC}	G_{IC}	σ_y	E
s	(MPa $m^{1/2}$)	(kJ m^{-2})	(MPa)	(GPa)
PE	0.65	0.30	130.6	1.42

- 5 -

			5	
HPE	0.98	0.64	131.0	1.50
			4	
ME	1.30	1.06	67.16	1.60
MEH	1.46	1.57	103.6	1.36
			2	

Table 1. Mechanical properties of epoxies prepared.

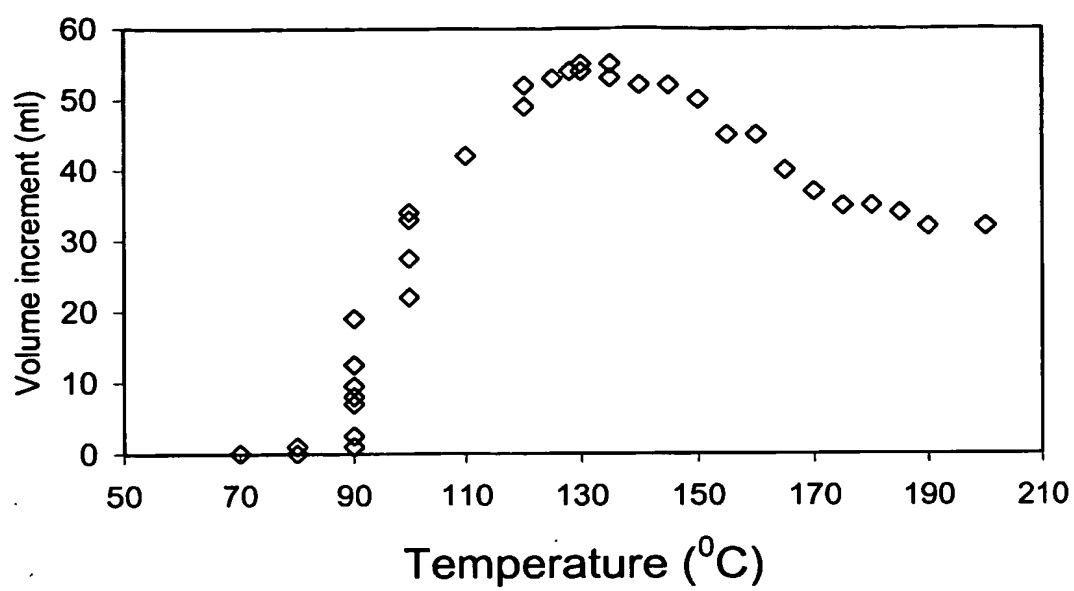
It has thus been found that epoxy resins toughened in this manner by the addition of expandable hollow microspheres and subsequently heated exhibit increased fracture toughness compared with simple epoxy resins of similar construction. It has been found that the heat treatment improves interfacial bonding between microspheres and the matrix. Compressive residual stress around microspheres, which may be responsible for the major toughening mechanism, is successfully created by hollow microspheres with the heat treatment. It has been found that specific fracture energy of epoxy can be increased about 13 times by this method.

- 6 -

CLAIMS:

1. A method of manufacturing a thermoset including the steps of adding expandable hollow microspheres to at least one of the base thermoset components in the liquid phase, and applying heat treatment to the liquid so formed, causing the microspheres to expand
5 during, or after, curing of the thermoset.
2. A method as claimed in claim 1 wherein the thermoset comprises an epoxy resin and the microspheres are added to the epoxy component.
3. A method as claimed in claim 2 wherein the mixture of epoxy component and microspheres are heated before adding a curing agent.
- 10 4. A method as claimed in claim 3 wherein the mixture is allowed to cool before adding the curing agent.
5. A method as claimed in either claim 3 or claim 4 wherein the mixture is stirred after adding the curing agent, and poured into a mould to cure.
6. A method as claimed in any one of the preceding claims wherein the microspheres
15 include a co-polymer shell and gas.

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**FIGURE. 1.**

INTERNATIONAL SEARCH REPORT

International application No.
PCT/AU03/00821

A. CLASSIFICATION OF SUBJECT MATTER		
Int. Cl. ⁷ : C08K 7/22, C08L 63/02, C08J 9/32, B29C 70/66		
According to International Patent Classification (IPC) or to both national classification and IPC		
B. FIELDS SEARCHED		
Minimum documentation searched (classification system followed by classification symbols) IPC: C08K 7/22, C08L 63/02, C08J 9/32		
Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched		
Electronic data base consulted during the international search (name of data base and, where practicable, search terms used) WPAT & JAPIO (search terms: thermoset, epoxy, microsphere)		
C. DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 5 712 317 A (MAKHLOUF et al.) 27 January 1998 See whole document	1-6
X	US 5 403 655 A (DEVINEY et al.) 4 April 1995 See whole document	1-6
X	US 5 385 778 A (DEVINEY et al.) 31 January 1995 See document	1-6
<input checked="" type="checkbox"/> Further documents are listed in the continuation of Box C <input checked="" type="checkbox"/> See patent family annex		
<p>* Special categories of cited documents:</p> <p>"A" document defining the general state of the art which is not considered to be of particular relevance</p> <p>"E" earlier application or patent but published on or after the international filing date</p> <p>"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)</p> <p>"O" document referring to an oral disclosure, use, exhibition or other means</p> <p>"P" document published prior to the international filing date but later than the priority date claimed</p> <p>"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention</p> <p>"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone</p> <p>"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art</p> <p>"&" document member of the same patent family</p>		
Date of the actual completion of the international search 16 July 2003		Date of mailing of the international search report 22 JUL 2003
Name and mailing address of the ISA/AU AUSTRALIAN PATENT OFFICE PO BOX 200, WODEN ACT 2606, AUSTRALIA E-mail address: pct@ipaustalia.gov.au Facsimile No. (02) 6285 3929		Authorized officer ALBERT S. J. YONG Telephone No : (02) 6283 2160

INTERNATIONAL SEARCH REPORT

International application No.

PCT/AU03/00821**C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT**

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 02/31077 A (HENKEL CORPORATION) 18 April 2002 See whole document	1-6
X	WO 02/24451 A (HENKEL CORPORATION) 28 March 2002 See whole document	1-6
X	WO 95/27000 A (PPG INDUSTRIES, INC.) 12 October 1995 See whole document	1-6
X	Derwent abstract accession no. 77355W/47, Class A94 (A21 A26), DT 2518825 (YOKOHAMA RUBBER KK) 13 November 1975 See abstract	1-6

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No.

PCT/AU03/00821

This Annex lists the known "A" publication level patent family members relating to the patent documents cited in the above-mentioned international search report. The Australian Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

Patent Document Cited in Search Report				Patent Family Member			
US	5712317	BR	9503539	CA	2186638	EP	753023
		US	5470886	WO	9527000		
US	5403655	US	5385778				
WO	200231077	AU	200196797	CA	2425414	US	2002115736
		US	6451876				
WO	200224451	AU	200191222	US	6403222		
WO	9527000	BR	9503539	CA	2186638	EP	753023
		US	5470886	US	5712317		
DE	2518825	JP	50141747				
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